

Metal Recovery/Removal Using Non-Electrolytic Metal Recovery

Minnesota Univ.-Duluth

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METAL RECOVERY/REMOVAL USING
NON-ELECTROLYTIC METAL RECOVERY

by

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report provides the results from a waste minimization research project for use by small and medium sized generators of hazardous waste. The purpose of the research is to develop and promote the use of innovative technologies and management practices to reduce or eliminate the generation of hazardous wastes. Waste minimization research is seen as one key way to help small businesses improve waste management practices by reducing liability, product costs, disposal costs, and environmental, health, and safety concerns.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

Radiator repair shops most commonly use hot caustic solutions to clean radiator sections prior to resoldering. The hot caustic, or "boil-out" solutions as they are called in the trade, become contaminated with dirt, rust flakes, paint flakes and miscellaneous particulate debris. In addition, the "boil-out" solutions dissolve lead, copper, zinc, and tin from the brass radiator components and the solder used for assembly. A portion of the dissolved heavy metals are in true solution whereas an important percentage precipitates as metal hydroxide, "quasi-colloids." Cooling the solutions and allowing the dissolved metals to precipitate and settle enables the operator to recycle up to 80 percent of the solution.

Preliminary test work has shown that sodium sulfide added to the caustic "enhanced sludge" solution will precipitate the metal hydroxides. The precipitates are coarse enough to settle out of the solution and leave a stripped, clarified liquid. This means that it should be feasible to design a precipitation and clarification system that could be used by any small radiator repair shop and eliminate this hazardous waste stream from the environment.

This work was performed between May 15, 1987, and June 30, 1988, at the University of Minnesota, Duluth.

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SECTION 1

INTRODUCTION

Throughout the automobile radiator repair industry, the hot caustic soda boil-out tank is one of the prime components of the repair line, in nearly every shop, whether large or small (see the review paper by Walters and Patterson (20)). In the U. S. and Canada, there are over 8,000 facilities which utilize the hot caustic tanks for radiator preparation. In addition, there are many other renovation industries which also utilize these units to clean/remove the paint, varnishes, oil, grease, dirt from the parts before rebuilding and refinishing; however, these parts are usually ferrous metal parts with only moderate amounts of non-ferrous metal components within the assembly, and are not considered in this study.

The automobile radiator, on the other hand, is almost entirely a composite of copper, lead, zinc and tin alloys. While most ferrous alloys are unaffected by a hot, caustic bath treatment, the copper and lead alloys of an automobile radiator are dissolved to a considerable extent during the hot caustic boil-out treatment. Walters indicates that radiator shops were exceeding the waste water discharge standards for lead, copper, and zinc (0.7, 4.5, and 4.2 mg/L, respectively). Tin was not indicated but these levels can range upward to approximately 2000 ppm in the caustic solutions.

A good overview of the automotive radiator repair procedure has been developed during the case study in Maryland by Walters and Patterson. The General Process Description and Block Flow Diagram of the process from their report is provided.

GENERAL PROCESS DESCRIPTION

A block flow diagram depicting the unit operations, sequence of work flow, and material flows in the radiator repair process is shown in Figure 1. The general process flow diagram shown in Figure 1 and variations in operating practices and conditions discussed here are based upon observations made during visits to eight shops in Maryland, in which shop owners were interviewed and process activities were observed. The magnitude of operation among these shops ranged from one person repairing one to two radiators per week to six people repairing as many as three hundred radiators per month.

As shown in Figure 1, radiators entering the process for repair are first drained to remove coolant (antifreeze and water) and transmission oil. This operation is somewhat variable in that radiators arriving at a given shop may already be drained of their contents and also because care is not necessarily taken to completely drain the radiator prior to the stripping process. Following draining, the radiator may be flow-tested to enable determination of the potential to restore the radiator, and to determine whether repair can be accomplished by normal means or whether physical cleaning (called rodding) may be necessary. The normal repair procedure involves submerging the radiator in a bath containing a caustic solution (often referred to as the boilout tank) which is heated to 140 to 200° F. The radiator is soaked in the bath for 15-60 minutes to soften and/or remove deposits, scale, corrosion and other foreign materials. Newer boilout tanks may also be equipped to enable ultrasonic cleaning, a technique which significantly improves cleaning efficiency. After

soaking, the radiator is withdrawn and to varying extents the contents are drained back into the boilout tank. Draining can range from a very limited effort on the part of the repair person to empty the radiator to a very thorough emptying including gravity draining of the bulk of the contents and use of compressed air to empty the oil cooling section of the radiator. At this point, the radiator has been surface-cleaned but is coated with the highly viscous contents of the boilout tank. The radiator is then rinsed using roughly 5 to 10 gallons of water per radiator in a rinse booth primarily to scour this coating from the inside and outside of the radiator. Rinsing is accomplished using either fresh tap water in a once-through system, wash water from a wash booth recirculation reservoir, or treated wastewater. The rinsed radiator is then leak-tested in a test tank. Leak-testing involves hooking up one end of the radiator to a compressed air line, plugging the other end, and submerging the radiator in the test tank. Any leak which is identified by visual detection or air bubbles is repaired typically by applying muriatic (hydrochloric) acid and/or flux followed by soldering. While repairs are being made the radiator is usually supported by a rack that is mounted directly over the test tank. Once the radiator has been repaired of all leaks, it is painted and reinstalled.

The contents of the boilout tank and test tank are originally prepared by adding boilout and test tank powders obtainable from numerous suppliers. The boilout powder consists essentially of NaOH, but may also contain chelating agents and surfactants. Typically, the boilout tank bath is prepared to initially contain 40 to 50 percent NaOH. The test tank powder contains fluorescein which, when dissolved in water, imparts a green color resembling that of antifreeze which aids visual identification of air bubbles generated during leak testing. The test tank powder also contains a buffer intended to counteract the effect of the excess muriatic acid which invariably is spilled and/or dripped from the radiator when it is being prepared for soldering.

The number and physical dimensions of the tanks in a shop vary depending upon the magnitude of operation and the types of radiators repaired (e.g., radiators for automobiles versus those for trucks and other heavy equipment). Of the eight shops surveyed in Maryland, most had one boilout tank ranging in size from as small as 70 gallons for ultrasonic cleaning tanks to as large as 600 gallons for a shop which frequently repairs truck and bus radiators. There are often two or more test tanks at a shop, and each has an average volume of about 180 gallons of water.

Wastes generated from the radiator repair process include rinse wastewater from the rinse booth, and sludge which must be periodically removed from the boilout tank. Some rinse booths are configured so that they discharge directly to the sewer, while others accomplish rinsing in a closed-loop system using rinse water from a reservoir. Wastewater volumes discharged by the former mode of operation are reviewed below. In the latter rinsing mode, wastewater and sludge are withdrawn from the reservoir on a periodic basis and combined with sludge removed from the boilout tank. Total sludge generation under either mode ranges from 30 to 300 gallons per year. The sludge is handled as appropriate under hazardous waste regulations.¹

¹Currently in Minnesota the disposal cost is in the range of \$175-\$225 per drum. This cost includes approximately \$25 for the shipping container (drum) and \$50-\$75 for the transportation as a hazardous material. Hazardous waste haulers consider the material primarily as a strong caustic solution and secondarily as lead-bearing material.

In addition to these wastes, most shops report the need for routine dumps of the boilout and test tanks. The need for dumping the boilout tank is based on the buildup of sludge in the bottom of the tank, and may be necessary once a year if sludge is not otherwise removed on a more frequent basis. Test tanks may be dumped as often as once per month owing to the buildup of suspended solids which impart turbidity to the water and interfere with the leak-test process.

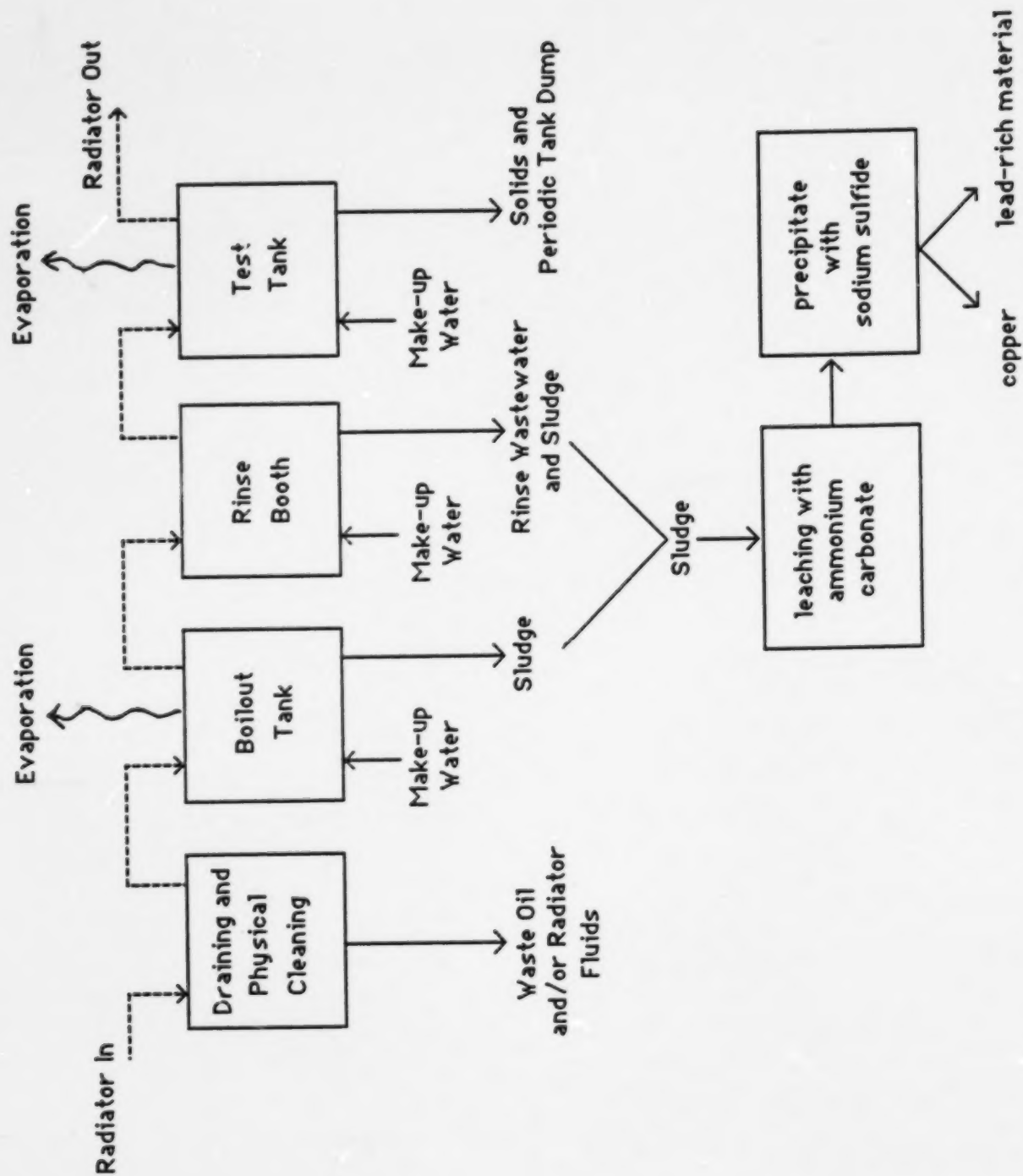
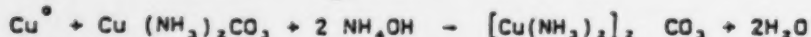
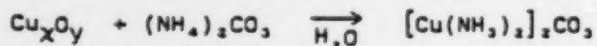


Figure 1. General Process Block Flow Diagram of the Radiator Repair Process.

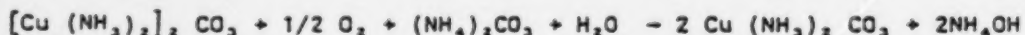
SECTION 2

DESCRIPTION OF PROJECT

The chemistry of the dissolution of copper oxides or copper metal by ammonia or ammoniacal solutions has been fairly well developed (3) for aqueous solutions. For the case of ammonium carbonate:

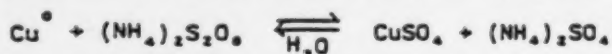


If adequate aeration is provided the cuprous solution will oxidize to the cupric state:



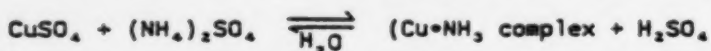
If adequate oxygen is available, a cyclic oxidation-reduction is set up limited only by the solution saturation of ionic copper or when the metallic copper completely dissolved.

Unlike ammonium carbonate, which is a salt formed from a weak acid and a weak base, ammonium persulfate is a salt formed from a strong acid and a weak base. Ammonium persulfate has been utilized in the electronics industry where a controllable etchant of moderate strength is required for printed circuit board manufacture. A possible dissolution reaction for metallic copper would be:



depending on dissociation coefficients.

A secondary reaction which forms an ammoniacal copper complex could be:



The copper complex would be analogous to $\text{Ca}(\text{NH}_3)_4^{+2}$ (16).

However, since the solution does not exhibit the brilliant blue color attributable to the presence of the copper-ammonium complex, it does not seem the equilibrium is toward the right. On the other hand, the solutions are only pale blue-green indicating that the equilibrium is toward the left and CuSO_4 seems to be the preferred ionic state "species."

There is a considerable body of literature concerning metal-ammonium complexes with both the alkali metals and base metals (1-3, 5-10, 12-17, 20, 21, 23). These papers provide an extensive insight into the physical nature of the metal-ammonium complex "ion/radical" state. In the paper by Bhattacharyya and Chen (4), there is an extensive overview of sulfide precipitation of metallic ions from aqueous solutions over a wide pH range.

However, radiator "boil-out" solutions are extremely caustic and range up to pH 13-14. The strong sodium and potassium base content would be expected to interfere with the chemical reactions developed under near neutral conditions; therefore, the processing chemical reactions were examined on a bench scale for

these radiator shop solutions. Within the guidelines of waste reduction and waste water minimization, large volumes of dilution water and wash water were purposely eliminated from the processes. In this regard, they are uniquely different from most mineral processing operations where large amounts of dilution and wash water are typical.

Thus, the objective of this study was to develop a simple concentration/precipitation/reduction technique which could function with these strong caustic solutions while minimizing large volumes of wash or dilution water during the operations.

SECTION 3

SUMMARY AND CONCLUSIONS

The results of the test work indicate that copper can be effectively separated from radiator boil-out tank sludge by a single leaching with ammonium carbonate. While some equipment and labor would be necessary, a large repair shop may be justified to do this procedure to provide an acceptable feed to a secondary lead refinery. Mr. John Tapper indicated that copper was the most undesirable tramp element in scrap lead materials and must be less than 0.02 percent in the refined lead ingot, which they produce (Appendix B).

While the ammonium carbonate leaching would be most effective on the earthy, sandy sludges produced by the traditional process, the sodium sulfide treatment would be most effective for the flocculent sludges produced in the ultrasonic boil-out tanks.

SECTION 4

RECOMMENDATIONS

Ammonium carbonate leaching of the sandy/earthy bottom sludge from radiator caustic "boil-out" tanks is effective to remove copper to leave a lead-rich sludge for secondary lead recovery. However, the process seems to involve more steps and procedures than a small/medium-sized radiator shop would be able to do in a cost effective manner. This would be a process more suitable for a collector/processor as a conditioning step to recover the copper and prepare the sludges for secondary smelting.

This intermediate processing is a research and development area which should not be ignored. Much of the current effort has been directed to the reduction of hazardous waste at the generator site for eventual hazardous waste landfill.

In the area of heavy metals, it may now be the time to begin implementation of the concepts: (a) Condition the heavy metal sludges for resource recovery at the generator level; and (b) Develop the processing technology for heavy metal resource recovery at the economics-to-scale for the intermediate collector and processor level.

In the area of municipal solid waste, resource recovery is becoming more commonplace as cleaned paper stock, high-value plastics, and glass are being separated from the MSW stream and returned to the marketplace as feedstock or energy commodities. Heavy metal sludges should be considered from this same resource recovery perspective.

SECTION 5

EXPERIMENTAL EQUIPMENT, MATERIALS AND PROCEDURES

Research was performed on three representative automobile radiator caustic "boil-out" samples. The samples represent the older operations and the newer technique combining an ultrasonic vibration tank with hot caustic solution. The lead content ranged from 8730 ppm to 4.8 pct. Analyses of the samples are shown with each sample for both caustic filtrate and the sludge bottoms.

CHARACTERIZATION OF SLUDGES

"B" Sludge/Liquid: This material was drawn from the bottom of a Jackson Ultrasonics, Inc. stainless steel, 23-gallon boil-out tank. The caustic solution was prepared with a proprietary radiator "boil-out" compound containing a large percentage of sodium hydroxide. This sample represents a low-metallic loading solution which has not had much contact time with the radiators being cleaned for repair. This solution probably just had additions of make-up water and chemical concentrate. The metal values of Pb, Cu, Zn, and Sn were determined to be 8730 ppm, 350 ppm, 462 ppm, and 2010 ppm respectively. Other components of this gelatinous sludge are as follows: Fe-112 ppm, Si-560 ppm, Ca-10 ppm, Mg-27 ppm, Na-49,500 ppm, K-410 ppm, P-2150 ppm.

"C" Sludge/Liquid: This material was drawn from the bottom of a Jackson Ultrasonics, Inc. stainless steel, 23-gallon boil-out tank. The entire 23 gallons of solution was drawn out and allowed to settle for about 60 hours, then decanted to concentrate the flocculent precipitate portion. The balance was returned to the boil-out tank along with additional water and caustic concentrate to make up a full tank. This sample contains the entire quantity of metallic sludge generated on this recycling-load batch process. The metal values (Pb, Cu, Zn, and Sn) of this gelatinous sludge were determined to be 17,500 ppm, 120 ppm, 980 ppm and 2,400 ppm respectively.

"D" Sludge: This material was drawn from the bottom of a conventional hot caustic radiator boil-out tank. This tank and ancillary equipment is typical of the conventional radiator repair equipment which represents the prevalent practice for many years. This sludge contains about 60% to 70% sandy and earthy solids with a small amount of dark coffee-colored liquid standing above. This sludge may be readily decanted and the active caustic solutions returned to the caustic tank for continued cleaning operations. Since this sludge was much like a mineral concentrate, it was analyzed as such. The primary metal species, Pb, Cu, Zn, and Sn, were determined to be 4.8 pct, 5.2 pct, 0.61 pct, and 6.1 pct respectively. The other inert mineral or gangue components were as follows: Fe-4.8 pct, SiO_2 -27.8 pct, Al_2O_3 -4.4 pct, CaO-5.0 pct, MgO-2.3 pct, Na_2O -6.5 pct, K_2O -0.72 pct, and P_2O_5 -0.33 pct.

The chemical analysis was performed on the liquid samples by atomic adsorption apparatus after suitable dilution and comparison to standard samples. The sandy/earthy sludges were much like ore/mineral samples and required a sodium peroxide fusion procedure before dissolution, dilution, and determination by atomic adsorption analysis. These procedures are provided in detail as a supplement to this report in Appendix C.

Although laboratory grades and quantities of chemicals were used for this

project, they would be available in bulk from an industrial chemical supplier. The prices quoted for these chemicals in bulk are as follows:

- Sodium Sulfide - \$47.75/hundred weight in 50 lb. bags
- Ammonium Carbonate - \$200/hundred weight in 110 lb. drums
- Ammonium Persulfate - \$92.50/hundred weight in 225 lb. drums

For comparison, these same chemicals run \$10-\$20 per pound for the same technical grade when procured through laboratory and scientific suppliers.

Most of the bench-scale leaching tests were performed in 1-liter plastic jars with a "U.S. Stoneware" jar mill to provide agitation, mixing, and blending between the leachate solution and the sludge sample. Vacuum filtration on the leach residue was accomplished with Buechner funnel and vacuum flask. In some instances, a centrifuge was required to remove the very fine sludge sediments from the analytical samples. The centrifuge speed was not critical; 10,000 to 15,000 RPM was adequate for separation.

SECTION 6

RESULTS AND DISCUSSION

Leaching tests have been performed to both test the effectiveness of ammonium persulfate and ammonium carbonate as a copper leachant and sodium sulfide as a copper precipitant. These tests (Table I) indicated that a significant amount of copper could be put into solution and the sodium sulfide would precipitate the ionic copper to leave a nearly copper-free filtrate. For instance, the solubility product for the resultant copper sulfide is: K_{sp} (Copper Sulfide) = 2.4×10^{-28} mol/liter in water. The resultant metallic ion concentration in the clear filtrate would be below detection limits of the analytical equipment, but the strong caustic soda solution interferes with the reaction equilibria.

AMMONIUM PERSULFATE LEACHING

Even though ammonium persulfate is known to exhibit good leaching properties for copper, it has not been particularly effective to selectively remove copper from these caustic sludges. The resultant leach solutions are a pale blue-green color which indicates the copper ion is present in a simple ionic state. It does not have the intense blue color of the copper-ammonium complex. The copper concentration is an order of magnitude lower than the ammonium carbonate leachates, also. The maximum concentration of copper attained for ammonium persulfate leaching was 1280 ppm as opposed to 10,600 ppm copper using ammonium carbonate under similar conditions.

A flow chart of an ammonium persulfate leaching scheme is shown in Figure 2 along with the analyses of some of the key intermediate products. Since ammonium persulfate does not seem to be an effective leaching agent under these high caustic conditions, it is not recommended for selective copper leaching from these caustic sludges.

AMMONIUM CARBONATE LEACHING

Ammonium carbonate seems to be an effective leachant to selectively remove copper from these caustic sludges. All leachates produced by ammonium carbonate exhibit the brilliant blue of the copper-ammonium complex and the copper concentration of the leachates have reached 10,600 ppm copper, while maintaining the lead levels below 100 ppm. A flow chart of an ammonium carbonate leaching scheme is shown in Figure 3 along with the analyses of some of the key intermediate products. This flow scheme goes beyond the scope of this project such that no products are sent to landfill or sewage treatment. It is a totally closed system with all products conditioned for delivery to a secondary metals recovery plant.

The copper extraction values are plotted in Figure 4 as a function of the ammonium carbonate or ammonium persulfate leaching reagent used to remove copper from radiator sludge "D". Ammonium carbonate seems to function quite effectively as a copper leachant in these strongly basic solutions. Copper extraction of 80 percent can be obtained without neutralization or optimization of the leachant-copper ratio. This is an important factor for a treatment process carried out by semi-skilled labor. On the other hand, the strong acid salt, ammonium persulfate, is not an effective copper leachant. This is perhaps due

Table I. Extraction of Heavy Metals by Ammonium Carbonate or Ammonium Persulfate Leaching

TEST	LEACHING REAGENT	REAGENT TO SLUDGE RATIO	LEACHATE CHEMICAL ANALYSIS										SLUDGE AFTER LEACH CHEMICAL ANALYSES				COPPER EXTRACTION DEGREE
			LEAD ppm	LEAD gm Units	COPPER ppm	COPPER gm Units	ZINC ppm	ZINC gm Units	TIN ppm	TIN gr Units	SODIUM ppm	LEAD percent	COPPER percent	ZINC percent	TIN percent		
	Ammonium Carbonate																
	Grass																
HEAD	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	4.8	5.2	0.61	6.1	M/A	M/A
1	5	1:10	71	0.014	5,020	1.004	50	0.010	<1	<1	10,500					38.6	
2	5	1:10	112	0.022	5,200	1.040	59	0.011	<1	<1	9,100					40.0	
3	10	2:10	56	0.011	8,800	1.760	140	0.028	<1	<1	9,700					67.7	
4	15	3:10	93	0.019	10,400	2.120	218	0.043	<1	<1	8,900	5.1	1.7	0.60	8.4	81.5	
5	20	4:10	134	0.027	10,400	2.080	282	0.056	<1	<1	10,800					80.0	
	Ammon. Persulfate																
1	5	1:10	5.4	0.0011	1,130	0.226	2.3	0.0005	<1	<1	11,400					8.7	
2	10	2:10	5.8	0.0012	1,240	0.248	7.8	0.0016	<1	<1	11,800					9.5	
3	20	4:10	17	0.0034	1,280	0.256	26	0.0032	<1	<1	9,300	4.9	5.1	0.64	7.3	9.8	

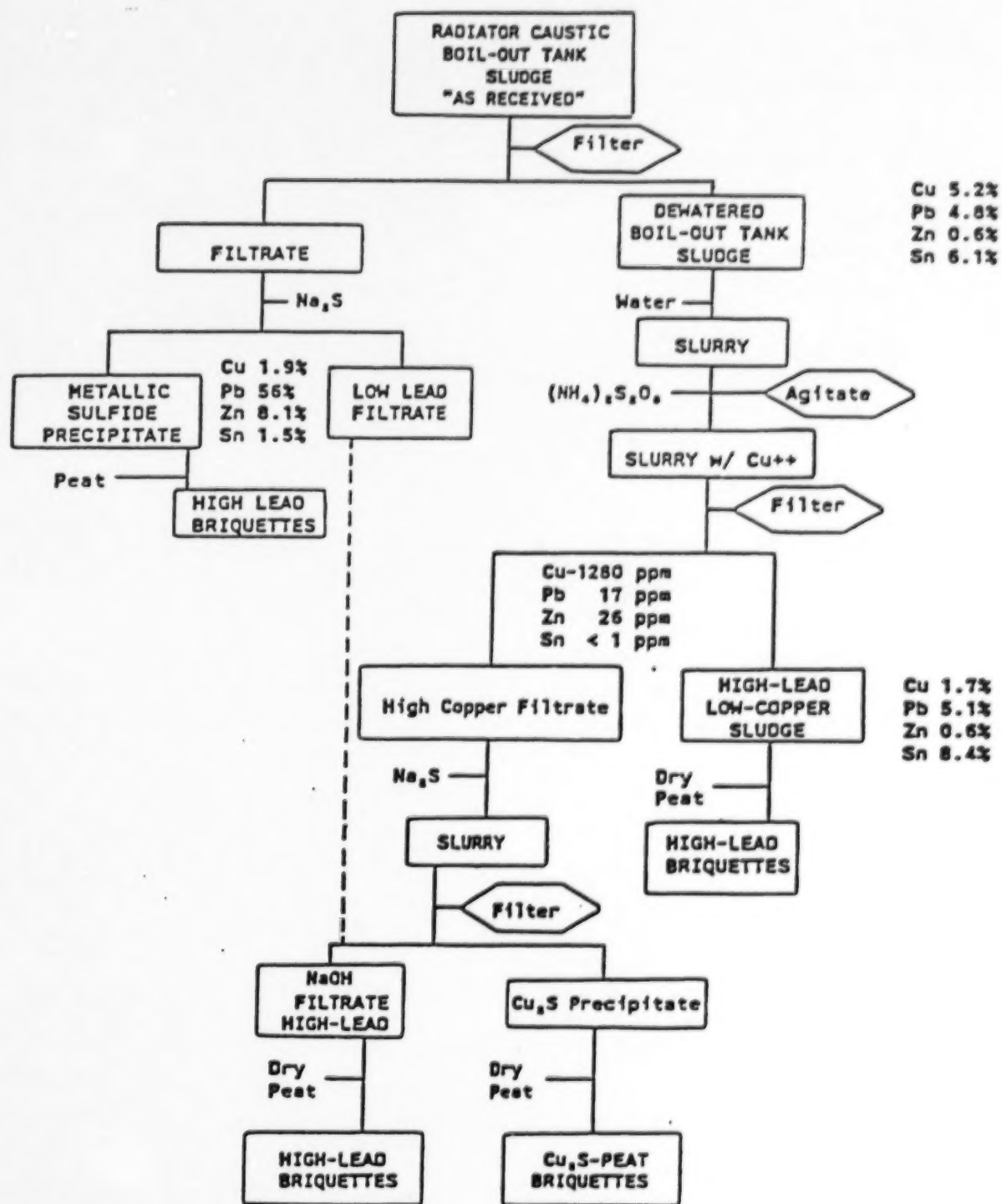


Figure 2. Ammonium Persulfate Leaching - Sodium Sulfate Precipitation Flow Chart.

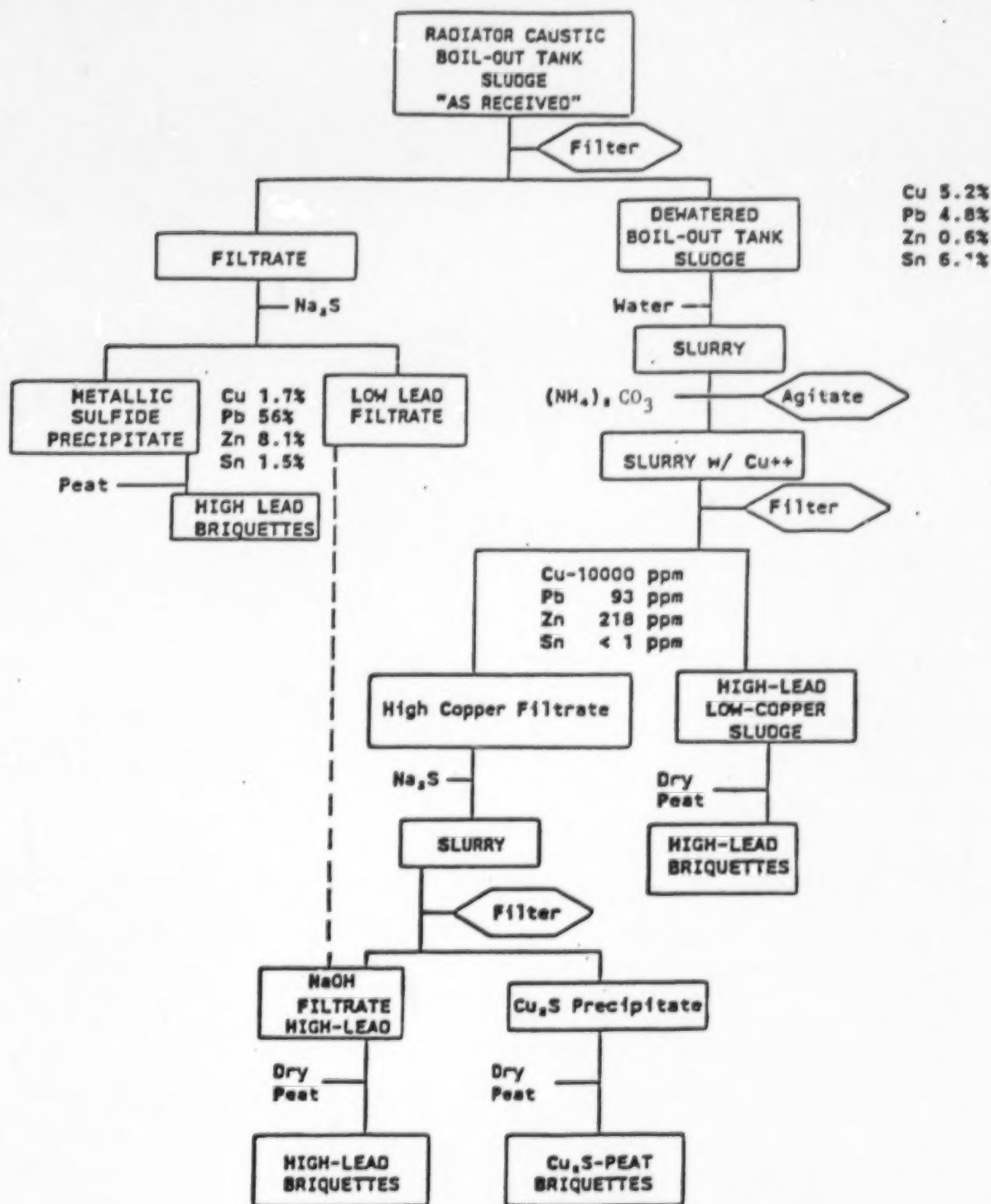


Figure 3. Ammonium Carbonate Leaching - Sodium Sulfide Precipitation Flow Chart.

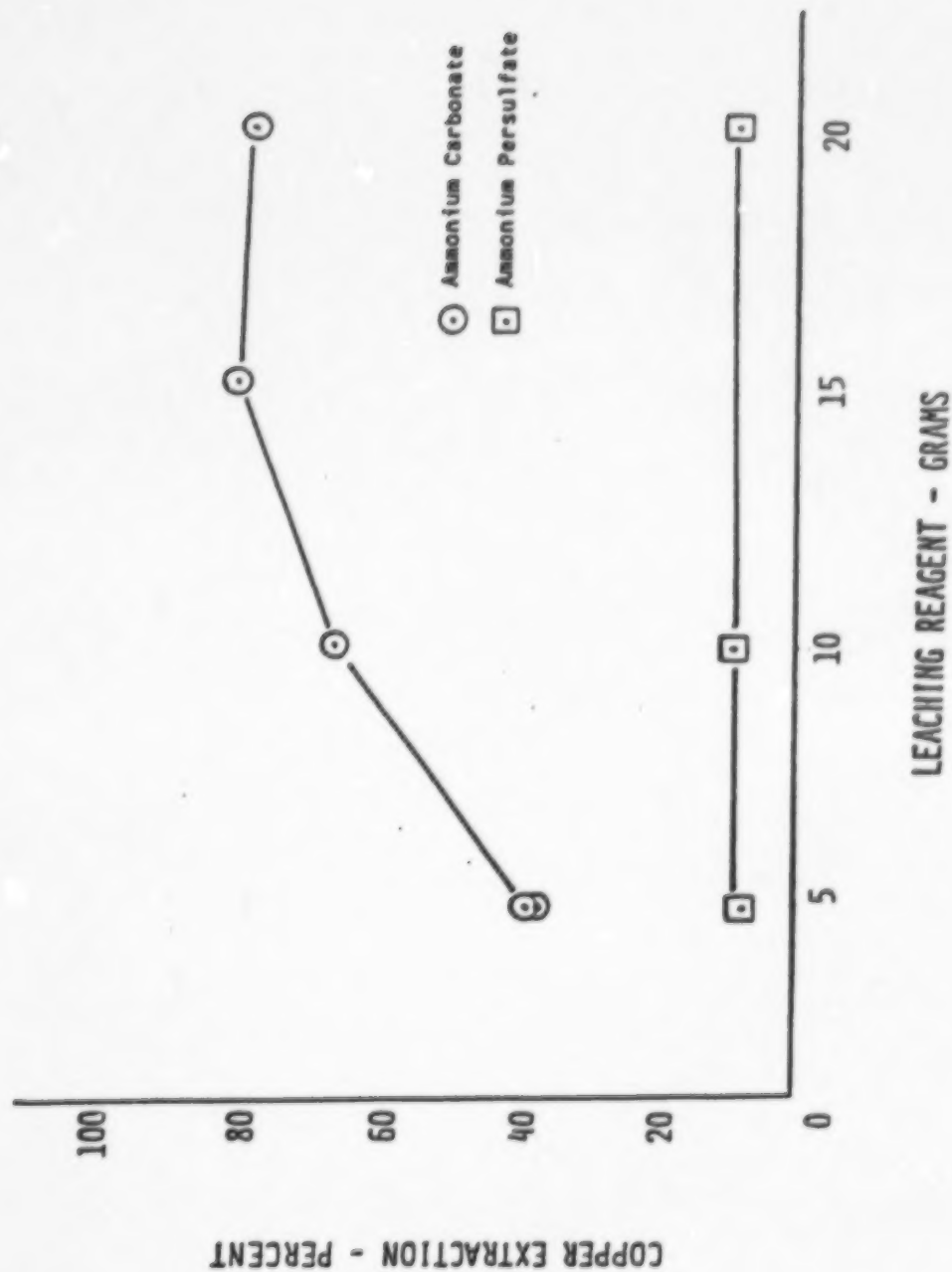


Figure 4. Copper Extraction from "D" Sludge with Ammonium Carbonate or Ammonium Persulfate

to a neutralization interaction of the persulfate radical and the strong caustic of the "boil-out" solution, but the mechanism has not been determined.

SODIUM SULFIDE PRECIPITATION

Due to the complexity of the selective leaching by a small generator, a much more simplified scheme has been developed to provide a marketable product for secondary metal recovery. Both the sludges produced in ultrasonic boil-out tanks had similar characteristics: flocculent precipitate, difficult to filter, difficult to settle, low-density precipitate. This type of "sludge" could be characteristic of all the stainless steel, ultrasonic, smaller "boil-out" units that are coming into the industry. A flow chart of this treatment scheme is shown in Figure 5 along with the analyses of the key intermediate products. The cooled caustic liquid/sludge is treated with sodium sulfide (Technical grade $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$) in a 1 to 20 weight ratio and stirred thoroughly to dissolve the sodium sulfide and allow the metallic sulfide precipitation to occur. The solubility products (in water) for the various resultant sulfides are as follows:

<u>Solubility Products</u>	<u>Ksp at 25°C</u>
Copper (I) Sulfide	$\text{Ksp} = 2.4 \times 10^{-28}$
Iron (II) Sulfide	$\text{Ksp} = 1.57 \times 10^{-19}$
Lead (II) Sulfide	$\text{Ksp} = 8.81 \times 10^{-28}$
Tin (II) Sulfide	$\text{Ksp} = 3.23 \times 10^{-28}$
Zinc (II) Sulfide	$\text{Ksp} = 2.91 \times 10^{-24}$

While the very fine black precipitate is difficult to filter, it settles quite readily and the liquid may be decanted or siphoned off the precipitate. In one case, the lead in the sludge was reduced from 8730 ppm to 11 ppm or a ratio of approximately 800:1. The resultant stripped liquor was reduced to 14 ppm combined Cu, Pb, and Zn. The tin, however, was not significantly reduced; i.e., 2010 ppm in the original liquid down to 1830 ppm in the final liquid. Apparently the caustic sodium level is so high that the amphoteric nature of the tin as sodium stannate $[\text{Na}_2\text{Sn}(\text{OH})_6]$ overrides the formation of tin sulfide.



In other words, the tin sulfide precipitation reaction is effectively inhibited by the high concentration of sodium hydroxide. Other means must be developed to remove the tin to the point where the resultant liquid may be sewered by the operator.

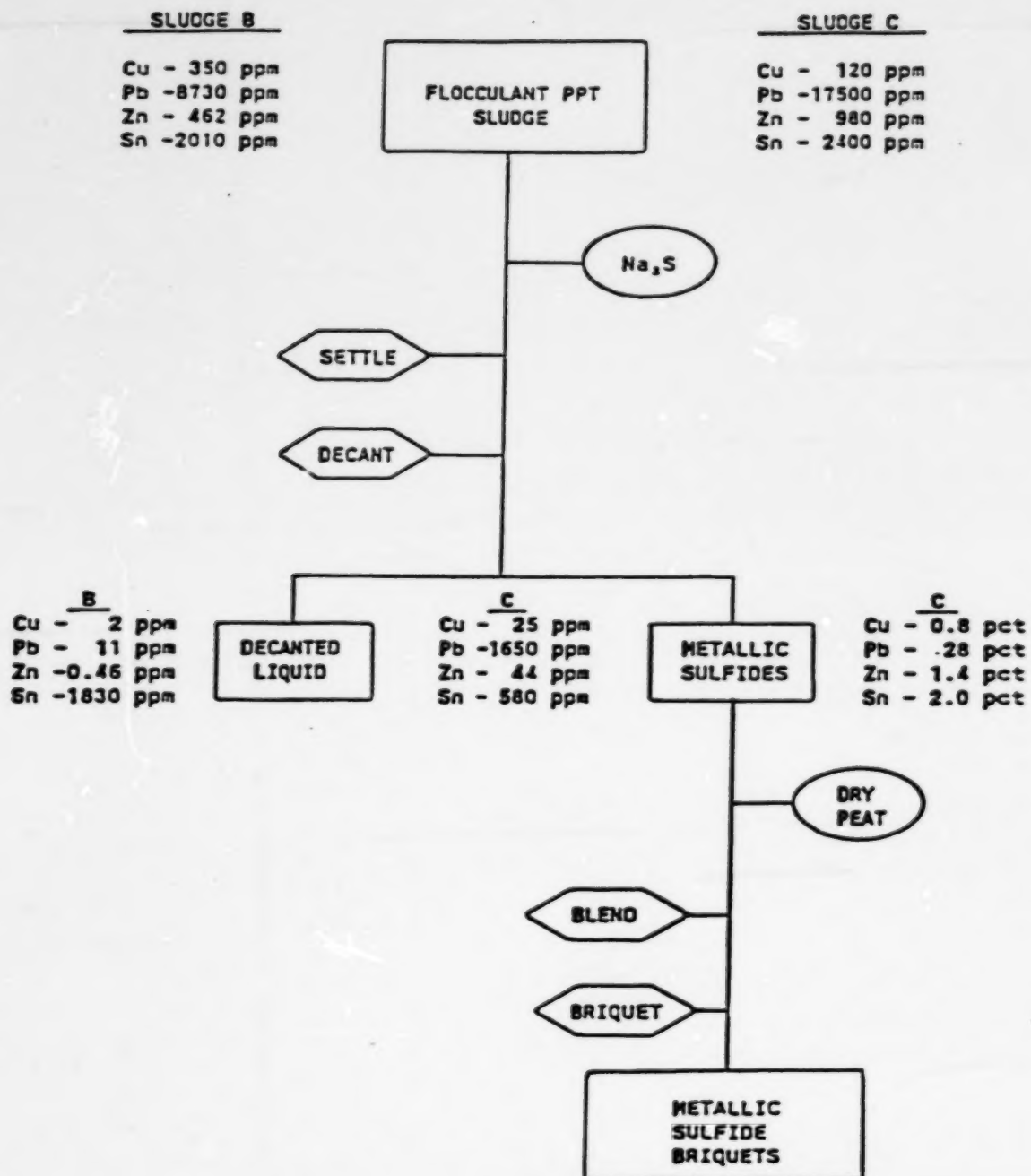


Figure 5. Sulfide Precipitation of Metallic Ions from Sludge Liquids.

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APPENDIX A

Proposed Scenario for Conditioning/Stabilizing Repair Shop "Boil-Out" Sludges for Metal Value Recovery

1. Damaged radiator admitted to the repair shop.
2. Damaged radiator water washed with medium pressure spray to remove dirt, organic debris, loose paint chips, some grease and oil.
3. Radiator boiled-out at approximately 170°F (75°C) in ultrasonic stainless steel tank with caustic solution to remove remaining paint/oil/grease/dirt, and chemically clean (etch) the brass surfaces for resoldering. Contact time: 1-2 hours each.
4. Process repeated with each radiator unit to be repaired. Additional water added to the tank to make up for drag-out losses adhering on each radiator and evaporation losses due to the high operating temperature of the caustic bath. Additional caustic chemical compound added as the chemical activity of the caustic bath diminishes based on the operator's experience of "acceptably clean" for the rest of the repair operations.
5. Caustic bath operates through the normal week load of five days, when the tank is completely drained into steel (non-galvanized or soldered) pails which are compatible with the heat and caustic content of the hot solution. These pails of high heavy-metal content solutions are allowed to cool and settle over the weekend (approximately 60-64 hours).
6. At the beginning of the next work week (Monday, A.M.), the pails of cold caustic solution are returned to the ultrasonic tank decanting them carefully to make a sharp separation between the liquid portion and the sludge portion. All the sludge portions are combined into one larger shipping drum with a minimum of rinse water to clean the pails.
7. Add several scoops of sodium sulfide to the sludge and stir with a paddle

or drill motor equipped with impeller to dissolve the sodium sulfide for reaction.

8. After one half to one hour, add several scoops of dry pulverized peat. Allow the drum to remain uncovered to promote atmospheric evaporation. Additional increments of dry peat should be added on a daily basis until all liquid is absorbed.
9. Repeat procedure each week until drum is filled and stabilized as a wet paste.
10. Seal drum securely and ship to secondary lead refiner as authorized by current regulations.

APPENDIX B

Smelter Response

Discussion with Mr. John Tapper, Chief Metallurgist, Gopher Smelting and Refining Company, 3385 Highway 149, Eagan, Minnesota.

The discussion centered around the smelting of peat compacts which had been impregnated with a mixture of heavy metal sulfides (high lead) from radiator caustic "boil-out" liquid sludges.

Gopher Smelting is a facility primarily engaged in breaking down spent lead-acid storage batteries and recovering the values; i.e., primary lead, antimony, polypropylene plastic, hard rubber chips and sulfuric acid. The plant is equipped to handle both the metallic lead from the grid plates and posts as well as the lead oxide/lead sulfate portion.

The primary operations of the plant are the lead reverberatory furnace, the lead blast furnace, and the battery breaking line equipped to provide a filter cake of lead oxide/sulfate and particulate lead materials. The plant is rated at 10,000 batteries per day or 100 tons per day refined lead and lead alloys. The plant is equipped with modern baghouse equipment and other reclaiming equipment to minimize the loss of lead into the surrounding area. The plant is "fully bonded and insured against sudden or gradual loss." Mr. Tapper mentioned that this was the only plant of this kind which is so insured.

Sample briquets were brought in to discuss reclaiming the lead and other heavy metals from the peat/metal sulfide briquets. The briquets were produced with bone dry peat screened at -16 mesh to remove woody matter. Sodium carboxy methylcellulose was dry mixed into the peat 10% by weight of the dry peat. The wet metal sulfide precipitate was blended into the dry peat at a ratio of 1.8

to 1. When fully blended into a thick paste, the briquets were formed in a 1" double piston die compressed at 20,000 lb. load. These samples were 1" dia. by 3" long when removed from the die. Some of the samples were air-dried while others were oven-dried at 45°C. Some shrinkage and cracking occurred during both drying modes, but had good handling strength in spite of the deep lateral shrinkage cracks. The nominal mixed metal sulfides analysis was Pb-56%, Cu-1.9%, Zn-8.1%, Sn-1.5% and approximately 50 wt. pct. of the dry peat briquet. No attempt was made to optimize the metal sulfides - peat - NaCMC ratio. The high peat - NaCMC portion insured that a strong briquet would be made for this demonstration.

Mr. Tapper examined the pellets carefully and indicated that such lead-containing briquets could easily be run through the blast furnace or reverberatory furnace to recover the lead while the peat would provide fuel value for the operation. While the finished refined lead must contain < 0.02 pct copper, he indicated that the tonnage of these briquets would be very small and the copper, tin, zinc content would either be diluted out or oxidized/slugged off into the baghouse dust or slag.

While the metallurgical concern or problems seemed to be minimal, he was concerned about the EPA operating permit which may prohibit the plant from running the lead-containing briquets. In the past, the plant was allowed to run their in-house lead-containing gloves, respirators, boots, pallets, etc. through the lead blast furnace/reverberatory to recover the lead content. They are not permitted to do so now because these items have been classed as "HAZARDOUS MATERIALS." The key issue is whether these briquets are classed as lead "scrap" or EPA listed "hazardous materials."

In summary, the Gopher Smelting and Refining Co. personnel were pleased with the stable, readily-handled, high-lead/peat briquets and were confident they could run them through their recovery furnaces if the EPA regulations would allow them to do so.

APPENDIX C

PROCEDURE FOR THE ANALYSIS OF SiO_2

Procedure

1. Weigh out 1.0000 gram pulverized sample of crude ore and brush into a 150-ml beaker.
2. Add approximately 30 ml of concentrated HCl , cover with a water glass and digest on the hot plate until all the soluble minerals are in solution, adding more HCl if necessary.
3. Oxidize by adding 5 ml of concentrated HNO_3 . Boil for approximately 5 minutes.
4. Add 10 ml of HClO_4 and bring to fumes. Fume for 5 minutes.
5. Cool, and dissolve the salts by adding 50 ml H_2O . Boil for a few minutes.
6. Filter - into a 400-ml beaker - using Munktells 11-cm OK papers.
7. Wash alternately with 1-1 HCl and H_2O until the yellow stain is no longer noticeable. Then wash twice with water.
8. For a complete analysis, reserve the filtrate for the determinations of Al_2O_3 , TiO_2 , CaO , and MgO .
9. Ignite the residue in a platinum crucible at 1000°C .
10. Cool in a desiccator and weigh. Record weight of residue plus crucible.
11. Treat the residue with 5 to 10 drops of 1-1 H_2SO_4 and fill the crucible to $3/4$ full with HF .
12. Evaporate to dryness on the hot plate.
13. Ignite as before, cool in a desiccator and reweigh.

APPENDIX D

14. The loss in weight (Step 10 minus Step 13) multiplied by 200 = percent SiO_2 .
15. When a complete analysis is to be determined on the sample, fuse the residue in the platinum crucible with a few grams of Na_2CO_3 or $\text{K}_2\text{S}_2\text{O}_7$, dissolve in 1-1 HCl and combine the solution with the filtrate in Step 8.

Solutions

1. HCl - concentrated
2. HF (48%)
3. HClO_4 (60%)
4. HCl - dilute (1-1)
5. H_2SO_4 - dilute (1-1)
6. HNO_3 - concentrated
7. Na_2CO_3 - salt
8. $\text{K}_2\text{S}_2\text{O}_7$ - salt

Standardization

Check the procedure periodically by including with the samples a known SiO_2 standard.